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(54) Polymer hydrogenation catalysts.

(57) The hydrogenation of unsaturated polymers is effected employing a heterogeneous catalyst comprising a Group VIII metal and a porous support wherein the porous support is characterized by a pore size distribution such that at least 95 percent of the pore volume is defined by pores having diameters greater than 450 Å (45 nm) and the ratio of metal surface area to carrier surface area is in the range of from 0.07 to 0.75:1. The catalyst is useful in selective polymer hydrogenations, such as are required in hydrogenating ethylenically unsaturated regions with a minimal amount of aromatic unsaturation hydrogenation. The catalyst is very active under mild temperature conditions, from room temperature to 140 °C.

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POLYMER HYDROGENATION CATALYSTS

The present invention relates to heterogeneous catalysts for hydrogenation of unsaturated polymers, particularly higher molecular weight polymers, e.g., having molecular weights in the range of from 65,000 to 500,000.

Polymers containing ethylenic and aromatic unsaturation such as styrene-isoprene-styrene and styrene-butadiene-styrene triblock copolymers have broad commercial use in adhesive formulations, footwear and as polymer modifiers. Such copolymers contain one unit of ethylenic unsaturation for each unit of diene in the final polymer. The ethylenic unsaturation provides sites for chemical reactions to occur making the polymer susceptible to thermal degradation, oxidative degradation, instability under ultraviolet radiation and general poor weatherability.

Polymers that have the ethylenically unsaturated region saturated via hydrogenation have greatly improved stability and weathering properties because the reactive site of ethylenic unsaturation is removed. Hydrogenation may also improve some of the physical properties of these polymers, see, for example, British Patent 1,229,573 and U.S. Patent 3,333,024. However, hydrogenation of the aromatic unsaturation can have deleterious effects on polymer properties, such as a loss of rubber-like characteristics. Thus, it is desirable that the hydrogenation be selective to saturation of the ethylenically unsaturated region with minimal hydrogenation of the aromatic region.

Both homogeneous and heterogeneous catalyst systems have been widely used for the hydrogenation of ethylenically unsaturated polymers. Homogeneous catalytic processes are disclosed in U.S. Patents 3,595,295; 3,595,942; 3,700,633 and 3,810,957, as well, as in "Polymer Hydrogenations With Soluble Lithium/Cobalt And Aluminum/Cobalt Catalysts"; J.C. Falck, Catalysis In Organic Synthesis, E.D. P.N. Rylander and H. Greenfield, Academic Press, New York, 1976, pp. 305-24. Homogeneous catalyts can be highly selective with respect to effecting hydrogenation of ethylenically unsaturated moieties. These catalysts exist in the same phase as the reaction mixtures, which makes their separation from the hydrogenated polymer difficult and adds significantly to process costs.

The heterogeneous catalysts, on the other hand, exist as a phase distinct from the reaction mixture, and their separation from the hydrogenated polymer is more easily accomplished. Unfortunately, extensive hydrogenation of the aromatic region typically occurs along with hydrogenation of the ethylenically unsaturated region when heterogeneous catalyst systems are used to hydrogenate the polymer. This is shown in a number of patents and confirmed by our studies on commercial catalysts, see U.S. Patents 3,333,024; 3,415,789; Belgium Patent BE871348 and British Patent GB 2,011,911.

Considerable research has been directed to the development of heterogeneous catalyst systems which would more selectively hydrogenate the ethylenically unsaturated region while reducing the hydrogenation of the aromatic region. One such approach is described in French Patent 2,468,618 (British equivalent GB 2,061,961). This patent describes the use of a 5 percent rhodium/activated carbon catalyst as a selective hydrogenation catalyst for a number of aromatic-diene copolymer systems. In particular, two examples are given of selective hydrogenation of triblock copolymers. Examples 3 and 8 of the French patent indicate selective hydrogenation with triblock copolymers whose molecular weight is 60,000. Our studies indicate that a 5 percent rhodium/activated carbon catalyst employing an activated carbon having an average particle size of 20 to 40 microns and a surface area of 1,100 square meters per gram has poor, nonselective activity for hydrogenation of a commercial styrene-butadiene-styrene block copolymer whose average molecular weight is 177,000. The poor activity is also independent of catalyst particle size with particle sizes as small as 5 microns. Although this catalyst may have some use for low molecular weight polymers, it is not useful for higher molecular weight polymers and falls outside the range of catalysts specified later in this invention.

A second approach which relates to a process for the selective hydrogenation of ethylenic-aromatic unsaturated polymer systems is described in U.S. Patent 4,501,685. This reference describes a system in which a poison is added to the feed to moderate the activity of the catalyst, thereby giving good selectivity for hydrogenation of the olefin region without hydrogenation of the aromatic region. The best results reported show that the aromatic hydrogenation is about one-half of the total hydrogenation, i.e., at 68 percent olefin hydrogenation, the aromatic hydrogenation is 34 percent. Extrapolating these results to almost quantitative conversion of the olefin would lead one to expect at least 50 percent hydrogenation of the aromatic region. This is not a very selective process. These is also a good possibility that some of the poison may end up in the polymer causing detrimental effects on its properties.

Another patent, U.S. Patent 4,560,817, describes selective hydrogenation catalysts for ethylenically-aromatic unsaturated polymer systems. This reference also describes the use of poisons to alter the

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selectivity of hydrogenation catalysts. Specifically, lithium methoxide ($LiOCH_3$) or ammonia are used as poisons to moderate the activity of the catalyst. For the reaction to be effective, the hydrogenation must be conducted at temperatures where polymer degradation occurs, e.g., 160 to 167° C. When the hydrogenation is effected at a lower temperature, e.g., 102° C., only a small amount of the unsaturation, in the range of 16 percent, is converted.

U.S. Patent 4,452,951 discloses a process for producing hydrogenated conjugated diene polymers employing a heterogeneous catalyst comprising porous silica having a specific surface area of not more than 600 square meters per gram and an average pore diameter of from 80 to 1,200 Å (8 to 120 nm) as a carrier for the hydrogenation catalyst, which can be any of the metallic or nonmetallic catalysts which have hydrogenating ability. The pore volumes which are recited appear to be a mix of calculated values, as in Example 1, and measured, as in Example 4. While the reference does teach catalyst supports having average pore diameters of 1200 Å (120 nm), it does not teach pore size distribution as an important criterion.

The heterogeneous catalyst systems of the present invention comprise a carrier having an actual or measured pore diameter of sufficient size to provide a pore size distribution such that at least 95 percent of the pore volume is defined by pores having diameters greater than 450 Å (45 nm). Preferably, 90 percent of the pore volume is made up of pores having diameters greater than 1,000 Å (100 nm) and most preferably, in the range of from 10,000 to 50,000 Å (1,000 to 5,000 nm). These are exceptionally large pores for catalyst carriers since artisans are conditioned to maximize surface area by using a carrier of significantly smaller pore size. In addition, U.S. Patent 4,452,951 teaches that the use of a support having average pore diameters exceeding 1,200 Å (120 nm) is so reduced in strength that it is broken during hydrogenation or catalyst separation and the separation of the catalyst becomes difficult.

A second requirement for the heterogeneous catalyst of the present invention is a very high ratio of metal surface area to carrier surface area. The ratio of metal surface area to carrier surface area of the present catalyst is in the range of from 7 to 75 percent, more preferably from 10 to 50 percent. This compares with the rhodium/activated carbon catalyst specified in GB 2,061,961 and the palladium/activated carbon catalyst in U.S. 4,501,685 which have metal surface areas of 0.5 to 1.5 percent of the surface areas of the support. This is also different from the palladium/alumina catalyst specified in U.S. Patent 4,560,817 which has maximum metal surface areas of 2 to 5 percent. The high surface area of the metal compared to the support gives a high metal site density on the catalyst. The extremely high metal surface area to the support surface area is in direct contradiction to the disclosure of U.S. Patent 4,337,329 which teaches, at column 2, lines 16 to 22, that if the amount of catalytic agent supported on the carrier is too large, dispersion of the metals on the carrier becomes poor, and the diameter of the metal particles increases to reduce the catalytic activity of the resulting catalyst.

This invention relates to the synthesis of unique heterogeneous catalysts for hydrogenation processes broadly and which are especially useful in selective polymer hydrogenations, such as are required in hydrogenating ethylenically unsaturated regions with a minimal amount of aromatic unsaturation hydrogenation. These catalysts are very active under mild temperature conditions, from room temperature to 140° C, but preferably from 50 to 110° C. The catalysts are capable of almost complete conversion of the ethylenic unsaturation region, in a range of from 90 to 100 percent, with minimum hydrogenation of the aromatic region from 0 to 25 percent, but typically about 7 percent. They are also useful for hydrogenation of copolymers with molecular weights ranging from 65,000 to 500,000, preferably in the range of from 150,000 to 500,000, and most typically around 175,000.

In the ensuing discussion, for simplicity and convenience, the invention has been directed as being applicable to the hydrogenation of polymeric materials containing both ethylenic and aromatic unsaturation. However, it should be understood that the invention is equally applicable to other unsaturated materials which normally would be subjected to hydrogenation with heterogeneous catalyst systems.

The unique heterogeneous catalyst compositions of the present invention comprise at least one Group VIII metal with palladium, rhodium ruthinium, cobalt, nickel and platinum being currently preferred, on a porous, powdery or granular carrier or support material.

Substantially any of the known heterogeneous catalyst carriers, such as diatomaceous earth, alumina, activated carbon, silica alumina or silica, can be employed in the practice of this invention; providing, however, that at least 95 percent of the pores have a measured pore diameter greater than 450 Å (45 nm) and, more preferably, that at least 90 percent of the pores have a measured pore diameter greater than 1,000 Å (100 nm), most preferably in the range of from 10,000 to 50,000 Å (1,000 to 5,000 nm). In this regard, it is pointed out that while there is no reason to exclude silica as an effective support for the current heterogeneous catalyst, none of the currently commercially available silicas are acceptable because their measured pore diameters are all too small and do not fit the foregoing measured pore diameters, that is,

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pore size distribution, limitations. However, there is no reason to suspect that a silica having the required measured pore diameter would not be acceptable. Providing that the support has the proper measured pore diameter, there is no particular other limitation to be imposed on it. Thus, appropriate supports include materials used for humidity control, moisture-proofing, gas chromatography, thin-layer chromatography, column chromatography and liquid chromatography. The supports may be powdery, spherical or molded.

Specific support materials are a diatomaceous earth support (Johns Manville Celite® F.C.); alumina (Rhone-Poulenc SCM 9x) and an activated carbon (City Service Raven MT-P). These supports have the following physical characteristics:

	Support		
	Johns Manville Celite F.C.	Rhone-Poulenc SCM-9X Al_2O_3	City Service Raven MT-P Carbon
Surface Area (m^2/g)	2.5-3.5	10-15	6-10
Pore Volume	1.8	0.7	0.4
Pore Distribution Å (nm)			
> 10,000 (1000)	99	15	7
1,000 to 10,000 (100 to 1000)	1	80	82
500 to 1,000 (50 to 100)		5	11
100 to 500 (10 to 50)			
20 to 100 (2 to 10)			
0 to 20 (0 to 2)			

Among supports which have been evaluated and found unsatisfactory are alumina (Calsicat SD and Norton 6175); silica (Davison 57) and activated carbon (Pittsburgh CPG). These supports have the following physical characteristics:

	Support			
	Calsicat SD Al_2O_3	Norton 6175 Al_2O_3	Davison 57 SiO_2	Pittsburg CPG Carbon
Surface Area (m^2/g)	30 to 40	230 to 290	275 to 325	900 to 1100
Pore Volume (cc/g)	0.8	0.9	1.1	0.8
Pore Distribution Å (nm)				
> 10,000 (1000)	1			
1,000 to 10,000 (100 to 1000)	22	8	1	12
500 to 1,000 (50 to 100)	36	3	3	10
100 to 500 (10 to 50)	40	21	80	9
20 to 100 (2 to 10)	1	68	15	27
0 to 20 (0 to 2)				42

Catalyst properties, e.g., particle size, porosity, pore dimensions and surface characteristics significantly affect heterogeneous-catalyzed hydrogenations. Typically, the majority of pore diameters referred to in heterogeneous catalyst references are calculated based upon the relationship that the pore diameter is substantially equivalent to the ratio of the pore volume to the surface are. Thus, assuming cylindrical pores, the pore diameter can be calculated in accordance with the equation

$$\text{PD (Pore Diameter)} = \frac{40{,}000 \times \text{Pore Volume (cc/g)}}{\text{Surface Area } (m^2/g)}$$

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It so happens that the calculated pore diameter is always larger than the actual measured pore diameter and the difference can and does significantly affect the peformance of the heterogeneous catalyst. This difference between calculated and actual or measured pore diameters is exemplified by a Davison LSA alumina support having a pore volume of 0.89 cc/gm and a surface area of 160 m^2/gm. Using the above equation for pore diameter (in Å), this support has a calculated pore diameter of (40,000) (0.89) ÷ 160 Å (16 nm) or 222.5 Å (22.25 nm). By porosimetry analysis following ASTM D-4284-83, 86.7 percent of the total surface area occurs in pores having diameters in the range of from 60 to 139 Å, (6 to 13.9 nm), which is substantially less than the calculated value of 222.5 Å (22.25 nm). The values specified for the heterogeneous catalyst supports of this invention are actual as opposed to calculated.

The various properties of the catalysts of this invention were measured by the following methods:

The average particle diameter of the support was determined from a particle diameter distribution curve prepared on the basis of its optical or electron micro photograph.

The specific surface area of the support was calculated by the BET (Brunauer-Emmett-Teller) method from the amount of nitrogen absorption measured by a low-temperature nitrogen absorption method. A particular procedure for determining surface area of catalysts is defined by ASTM D-3663-84.

The average pore diameter and pore volume of the support were measured by using a mercury porosimeter following the procedure of ASTM D-4284-83.

The degree of hydrogenation of the carbon-carbon double bonds was measured by an iodine value method.

It should be noted that the pore diameters are volume weighted pore diameter, i.e., the pores make up most of the volume, rather than surface weighted pore diameters, i.e., the pores make up the bulk of the surface area.

The metal surface area was measured by the chemisoportion technique described in J. LeMaitre et al, "Characterization of Heterogeneous Catalysts", Francis Delannay ed., Marcel Dekker, New York (1984), pp. 310-324. Metal surface area of catalysts can also be determined by chemisorption following the procedure of ASTM D=3908-2.

The catalytic metals used for these applications depend upon the exact nature of the material being hydrogenated. Generally, the catalytic materials will be taken from the metals of Group VIII of the periodic table with palladium, rhodium, ruthenium, cobalt, nickel and platinum being particularly preferred. The catalyst can be made form any compound containing these elements or any combination of these elements. Promoters can also be added to these catalyst to further enhance their selectivity in some reactions.

The heterogeneous catalysts of the invention can be prepared by forming a dispersion or solution of the catalytic metal or a metal compound such as a metal salt in an appropriate solvent media, such as water or an alcohol, combining the solution or dispersion of metal with the support material and removing solvent media to obtain a composite of the support and metal or metal compound. Representative nonaqueous diluents include the lower alkanols having up to 5 carbon atoms, such as, for example, methanol, ethanol and propanol.

After impregnation of the support from a nonaqueous solution of hydrogenation metal or metal components, excess diluent is removed and the impregnated support is activated by reducing at an elevated temperature and for a period of time sufficient to convert substantially all of the metal to active metal. The activation step is typically carried out by contacting the composite with a reducing gas comprising hydrogen. The reducing gas can be conveniently diluted with an inert gas such as nitrogen. The temperatures at which the activation takes place are typically in the range of from 150 °C to 500 °C., more preferably from 200 °C to 400 °C. After activation, the heterogeneous catalyst will contain a metal surface area based on the total surface area of the catalyst support, in the range of from 7 to 75 percent, preferably from 10 to 50 percent.

The catalysts of this invention can be employed for the hydrogenation of any unsaturated organic compound, including both monomeric and polymeric compounds. It is particularly suited for the hydrogenation of unsaturated polymeric material, particularly such polymers having molecular weights in the range of from 50,000 to 500,000, and especially from 150,000 to 500,000, and most typically 175,000. An especially attractive use for the heterogeneous catalyst systems of the invention is in the hydrogenation of high molecular weight unsaturated polymers which contain both ethylenic unsaturation and aromatic unsaturation because of their ability to hydrogenate substantially all of the ethylenic unsaturation without causing significant reduction in the aromatic portion of the polymer. Typically, the catalysts of this invention provide from 90 to 100 percent conversion of the ethylenic unsaturation and will cause less than a 25 percent, and usually in the range of from 0 to 7 percent, conversion of the aromatic unsaturation.

The catalyts of the invention are effective for the selective hydrogenation of the carbon-carbon ethylenic bonds in a copolymer of a conjugated diene and one or more copolymerizable monomers by a process

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which comprises hydrogenating the unsaturated polymer at a temperature in the range of from 50 to 150° C and at a pressure of hydrogen in the range of from 50 to 1,250 psig (350 to 8750 kPa gauge). The practice of the invention is particularly suitable for use with polymers containing olefinic unsaturation, which can be either quenched or living polymers. Preferably, the olefin- containing polymer feeds are diene-containing polymers and copolymers with vinyl aromatic/diene copolymers being most preferred.

Useful diene moieties include any conventional polyunsaturated monomers having from 3 to 12 carbon atoms. Butadiene is preferred. Useful aromatic monomers include mono- and polyvinyl-substituted aromatic compounds. Styrene, alpha-methylstyrene, acrylonitrile, metha-acrylonitrile and divinyl benzene are currently preferred monomers. Mixtures of vinyl aromatic and/or diolefin monomers can be used along with the optional inclusion of conventional olefinic monomers of other types in the preparation of the olefin-containing polymers. Specific examples of olefinic unsaturated polymers include polyisoprene, polybutadiene, styrene-butadiene copolymer, acrylonitrile-butadiene copolymers, acrylonitrile-styrene-butadiene copolymers, styrene-isoprene-styrene triblock copolymers and styrene-butadiene-styrene triblock copolymers.

The olefin-containing polymer may be hydrogenated as such. Preferably, the polymer is used in the form of a solution. The concentration of the polymer solution is 1 to 70 percent by weight, preferably 1 to 40 percent by weight. Any solvent which does not adversely affect the catalyst and can dissolve the polymer to be hydrogenated may be used to provide the polymer solution. There may usually be employed benzene, toluene, xylene, decalin, hexane, cyclohexane, tetrahydrofuran, acetone, methyl ethyl ketone, ethyl acetate and cyclohexanone. When the polymer is prepared by a solution-polymerization method, the resulting solution may be used as such for hydrogenation.

After hydrogenation, the heterogeneous catalyst is separated from the solution of the hydrogenated polymer by conventional methods such as precipitation, centrifugal separation or filtration. The hydrogenated polymer is then separated from the solution by usual methods for recovering a polymer from a polymer solution. For example, the separation can be effected by steam precipitation method which comprises contacting the polymer solution directly with steam, a drum drying method which comprises dropping the polymer solution onto a heated rotating drum to evaporate the solvent, or a method which comprises adding a nonsolvent to the polymer solution to precipitate the polymer. Hydrogenated polymers so separated from the solution are then subjected to a drying step involving water removal, hot air drying, vacuum drying or extrusion drying and then recovered as a solid product.

The resulting hydrogenated polymeric materials can be used in a wide range of applications because of the excellent weatherability, ozone resistance, thermal stability and cold resistance.

The following examples illustrate the present invention more specifically. It should be understood that the invention is not limited to these examples.

Example 1 - Preparation and Use of A Rhodium-Diatomaceous Earth Catalyst

An impregnating solution was prepared by dissolving 1.25 grams of hydrated rhodium trichloride in 34 mL of water. This solution was added to 10 grams of dried diatomaceous earth support (Johns Manville Celite™ F.C.) having a mean particle size of 5 micrometers, a surface area of 2.5 to 3.5 square meters per gram, a pore volume of 1.8 centimeters per gram and a pore distribution wherein 1 percent of the pores have a pore diameter in the range of from 1,000 to 10,000 Å (100 to 1,000 nm) units and 99 percent of the pore diameters are greater than 10,000 Å (1000 nm). The impregnated support was then dried and reduced to provide a catalyst having a rhodium concentration of 5 percent by weight. Hydrogen chemisorption gave a value of 0.77 H/Rh which corresponds to a metal surface area of 1.7 m^2/g of catalyst or 33 m^2/g of Rh. The metal surface area was 70.8%. A 2 gram sample of the heterogeneous catalyst was added to a reactor containing 15 grams of a styrene-butadiene-styrene triblock copolymer (Shell Kraton® D-1102) dissolved in 200 mL of cyclohexane. the hydrogenation was carried out, at about 97° C for 16 hours at 750 psig (5250 kPa gauge). The resulting copolymers showed greater than 95 percent hydrogenation in the olefin region and about 15 percent hydrogenation in the aromatic region.

Example 2 - Preparation and Use of A Palladium On Diatomaceous Earth Heterogeneous Catalysts

An impregnating solution was prepared by dissolving 0.83 grams of palladium chloride in 34 mL of water. This solution was added to 10 grams of the same diatomaceous earth support employed in Example 1. The impregnated support was then dried and reduced to provide a catalyst having a palladium

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concentration of 5 percent by weight. Hydrogen chemisorption gave a value of 0.038 H/Pd which corresponds to a metal surface area of 0.85 m^2/g of catalysts or 17 m^2/g of Pd. The metal surface area was 35.4 percent. A 1 gram sample of the catalyst was added to a reactor containing 17 grams of a styrene-isoproene-styrene triblock copolymer (Shell Kraton® D-1107) dissolved in 255 mL of cyclohexane. The hydrogenation was carried out at 90°C for 20 hours and the resulting polymer showed 92 percent hydrogenation of the olefin present and 1 percent hydrogenation of the aromatic region.

Example 3 - Effect Of Metal Surface Area On Catalyst Activity

A 5 percent platinum on diatomaceous earth (Johns Manville Celite® F.C.) catalyst was made following the procedure of Example 2 employing hexachloroplatinic acid as the precursor. The support had a mean particle size of 5 microns and a surface area of 2.4 m^2/g. Hydrogen chemisorption gave a value of 0.1 H/Pt which corresponds to a metal surface area of 1.3 m^2/g of catalyst or 26 m^2/g of Pt. The metal surface area was 54 percent. One gram of this catalyst was used to hydrogenate 17 grams of a styrene-isoprene-styrene triblock copolymer dissolved in 260 mL of cyclohexane at 83°C for 16 hours. The resulting polymer showed 97 percent olefin hydrogenation and 6 percent hydrogenation of the aromatic region.

A similar catalyst was made using the same support and the same platinum precursor, but the Pt concentration was 0.1 percent. Hydrogen chemisorption of this catalyst gave a value of 0.38 H/Pt which corresponds to a metal surface area of 0.094 m^2/g. The metal surface area was 3.9 percent. Fourteen grams of this catalyst were used to hydrogenate 17 grams of the same copolymer under the same conditions. The resulting polymer showed only 8 percent olefin hydrogenation.

The data show that the activity of catalysts with the same total metal surface

$(1.0\ g)\ (1.3\ m^2/g)\ =\ 1.3\ m^2\ =\ (14\ g\ (0.094\ m^2/g)$

is significantly affected by the percent surface coverage.

Example 4 - A Comparative Example Employing Catalysts Having A Pore Distribution Outside The Invention

Catalyst 4-1: A commercially available activated carbon (Calgon CAL) having a surface area of 825 m^2/g, a pore volume of 0.64 mL/g, an average pore diameter of 18 Å (1.8 nm) and a mean particle size of 10 was impregnated with an aqueous solution of palladium chloride and then reduced to give a catalyst having a palladium concentration of 5 percent by weight.

Catalyst 4-2: A commercially available alumina (Davison Low SA) having a surface area of 125 m^2/g, a pore volume of 0.9 mL/g, an average pore diameter of 288 Å (28.8 nm) and a mean particle size of 20 micrometers was impregnated with an aqueous solution of palladium chloride and then reduced to give a catalyst having a palladium concentration of 1 percent by weight.

Catalyst 4-3: A commercially available silica (Davison Grade 57) having a surface area of 157 m^2/g, a pore volume of 1.04 mL/g, an average pore diameter of 266 Å (26.6 nm) and a mean particle size of 20 micrometers was impregnated with an aqueous solution of palladium chloride and then reduced to give a catalyst having a palladium concentration of 1 percent by weight.

Catalyst 4-4: A commercially available copper chromite catalyst (Harshaw 0202) having a surface area of 48 m^2/g, a pore volume of 0.19 mL/g, an average pore diameter of 158 Å (15.8 nm) and a mean particle size of 20 micrometers.

A two gram sample of each catalyst was added to individual solutions containing 15 grams of a styrene-isoprene-styrene triblock copolymer (Shell Kraton® D-1107). In each case, the hydrogenation was carried out at 750 psig (5250 kPa gauge) for 20 hours at 90°C. The results were as follows:

Catalyst	% Olefin Hydrogenation
4-1	3%
4-2	5%
4-3	7%
4-4	less than 1%

The data demonstrate that catalysts having pore size distributions such that more than 80 percent of

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the pores have diameters below 500 Å (50 nm) are ineffective in hydrogenating higher molecular weight unsaturated polymers.

Example 5

The catalyst of Example 2 was used to hydrogenate 15 grams of polybutadiene dissolve in 250 m^2 of cyclohexane. The hydrogenation was carried out at 75 °C for 4 hours at 750 psig (5250 kPa gauge) using 1 gram of the catalyst. The resulting polymer showed 99 percent olefin hydrogenation.

Example 6

An aluminum oxide support (Rhone-Poulenc SMC-9X) having a surface area of 10 to 15 m^2/g, a pore volume of 0.7 cc/g, a pore distribution wherein 5 percent of the pores have a pore diameter in the range of from 500 to 1,000 Å (50 to 100 nm), 80 percent of the pores have a pore diameter in the range of from 1,000 to 10,000 Å (100 to 1,000 nm) and 15 percent of the pores have a pore diameter greater than 10,000 Å (1,000 nm) and an averge particle size of about 25 micrometers was impregnated with an aqueous solution of hexachloroplatinic acid, dried and reduced to provide a catalyst having a platinum concentration of 5 percent by weight. Hydrogen chemisorption gave a value of 0.088 H/Pt which corresponds to a metal surface area of 1.1 m^2/g of catalyst or 21 m^2/g of Pt. The metal surface area of this catalyst was 9 percent. A 1.5 gram sample of the thus-prepared heterogeneous catalyst was added to a reactor containing 17 grams of a styrene-isoprene-styrene triblock copolymer (Shell Kraton®) D-1107) dissolved in 250 grams of cyclohexane. The hydrogenation was carried out at 88 °C for 20 hours at 750 psig. The resulting polymer showed 91 percent olefin hydrogenation and 25 percent aromatic hydrogenation.

Claims

1. A catalyst comprising at least one Group VIII metal deposited on a porous support material, characterized in that said carrier has a pore size distribution such that at least 95 percent of the pore volume is defined by pores having diameters greater 45 nm (450 Å) and the ratio of metal surface area to carrier surface area is in the range of from 0.07 to 0.75:1.

2. A catalyst composition as claimed in Claim 1 wherein at least 90 percent of the pore volume of said carrier is made up of pores having diameters greater than 100 nm (1,000 Å) and the ratio of metal surface area to carrier surface area is in the range of from 0.1 to 0.5:1.

3. A catalyst composition as claimed in Claim 1, 2 or 3 wherein said carrier material comprises a diatomaceous each having a pore distribution wherein at least 90 percent of the pore volume is made up of pores having diameters greater than 1,000 nm (10,000 Å).

4. A catalyst composition as claimed in Claim 1, 2 or 3 wherein said carrier material comprises alumina wherein at least 90 percent of the pore volume of said alumina is made up of pores having diameters greater than 100 nm (1,000 Å).

5. A catalyst composition as claimed in Claim 1, 2 or 3 wherein said carrier material comprises an activated carbon wherein 100 percent of the pore volume is defined by pores having diameters greater than 500 Å.

6. A process for the hydrogenation of unsaturated polymeric materials comprising contacting at least one unsaturated polymeric material having at least one carbon-carbon double bond with hydrogen in the presence of a catalyst comprising at least one Group VIII metal impregnated on a pore support, said support having a pore size distribution such that at least 95 percent of the pore volume is made up of pores having diameters greater than 45 nm (450 Å), and the ratio of the metal surface area of said catalyst to the carrier surface area is in the range of from 0.07 to 0.75:1.

7. A process as claimed in Claim 6 wherein said support has a pore size distribution such that at least 90 percent of the pore volume is made up of pores having diameters greater than 100 nm (1,000 Å).

8. A process as claimed in Claim 6 or 7 wherein the ratio of the metal surface area of said catalyst to the carrier surface area is in the range of from 0.1 to 0.5:1.

9. A process as claimed in Claim 8 wherein said Group VIII metal is palladium, platinum or rhodium, said porous carrier comprises diatomaceous earth, alumina or activated carbon and said polymeric material comprises polybutadiene, a styrene-butadiene copolymer, a styrene-butadiene triblock copolymer or a

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styrene-isoprene-styrene triblock copolymer.

10. A process as claimed in Claim 9 wherein said diatomaceous earth has a pore size distribution such that at least 90 percent of the pore volume is made up of pores having diameters greater than 1,000 nm (10,000 Å), said alumina has a pore size distribution such that at least 90 percent of the pore volume is made up of pores having diameters greater than 1,000 Å and said activated carbon is characterized by pore size distribution such that at least 90 percent of the pore volume is made up of pores having diameters greater than 50 nm (500 Å).

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(54) Polymer hydrogenation catalysts.

(57) The hydrogenation of unsaturated polymers is effected employing a heterogeneous catalyst comprising a Group VIII metal and a porous support wherein the porous support is characterized by a pore size distribution such that at least 95 percent of the pore volume is defined by pores having diameters greater than 450 Å (45 nm) and the ratio of metal surface area to carrier surface area is in the range of from 0.07 to 0.75:1. The catalyst is useful in selective polymer hydrogenations, such as are required in hydrogenating ethylenically unsaturated regions with a minimal amount of aromatic unsaturation hydrogenation. The catalyst is very active under mild temperature conditions, from room temperature to 140° C.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 762 956 (X.LIU ET AL.) * abstract * * * column 2, line 16 - line 32 * *	1,2,4	C 08 C 19/02 C 08 F 8/04 B 01 J 32/00 B 01 J 35/10
X	EP-A-0 210 514 (EC ERDÖLCHEMIE GMBH) * page 11 - page 12; table 1 * *	1,2,4,5	
X	US-A-3 859 377 (D.E.GROSS ET AL.) * abstract * * * column 2, line 39 - line 49 * * * column 7, line 31 - line 35 * *	1-3	
X	DE-A-3 227 650 (NIPPON ZEON CO.) * claim 1 * * * page 10; example 4 * * * page 13 - page 14; table I * *	1,2,6-8	
A	DE-A-3 227 650 (* page 6, line 1 - line 18 *)	9	
D	DE-A-3 227 650 (& US-A-4 452 951)		
D,A	US-A-4 560 817 (R.L.BOBSEIN ET AL.) * column 5, line 5 - line 20 * *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
C 08 C C 08 F B 01 J

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	06 November 91	METTLER R.M.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
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E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

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